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STABILIZATION OF VEGETABLE OIL-BASED QUENCHANTS TO THERMAL-OXIDATIVE DEGRADATION: EXPERIMENTAL STRATEGY AND EFFECT OF OXIDATION ON QUENCHING PERFORMANCE

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ABSTRACT

Although petroleum oils continue to be the dominant type of basestock for the formulation of vaporizable quenchants, there is increasing pressure to identify an alternative basestock to address the limitations to their continued use because they are not a renewable basestock and they possess generally poor toxicity and biodegradability properties. Currently the most often cited alternative basestocks are those based on seed oils since they are renewable and usually non-toxic but especially because they are typically readily biodegradable. However, they suffer a critically important deficiency in that they are also typically much less stable to thermal-oxidative degradation than petroleum oils. There have been various reports discussing the effect of vegetable oil structure on oxidation and on the use of oxidation inhibitors to provide the necessary stabilization. However, most of these reports do not detail the experimental strategies used to provide this assessment and generally they do not address the relative effects of specific antioxidant structures on inhibiting oxidation and on quenching performance. This paper will address the experimental strategies used to determine the optimal antioxidant structure and concentration on properties and thermal-oxidative stability of seed oil derived quenchants and the effect of oxidation on quenching performance.

KEYWORDS: Vegetable oils; Antioxidants; Quenchants; Cooling Curve Analysis

INTRODUCTION

Quenchants not only control properties but also, depending on the quenching process and quenchant selection, control the residual stress profile with the steel and are critically important to optimize distortion control and prevent cracking. Depending on the steel and hardening process, the most common quenchants include are: oil, water, brine, aqueous polymer solutions and high-pressure gas quenching. Of the vaporizable quenchants, petroleum oil derived fluids are the most commonly encountered throughout the industry. However, there is an on-going effort to replace petroleum oil derived industrial fluids because of: price and the environmental and toxicological properties hazards exhibited by petroleum products.

Over the years, various quenching media have been evaluated as alternatives to oil including water, especially utilizing water in conjunction with time quenching [1] or by intensive quenching [2], aqueous polymers [3], and high-pressure gas [4]. However, petroleum oil derived quenchants still dominate the marketplace.

Currently, there is increasing interest in the use of biobased oils as replacements for petroleum oil basestocks. Biobased oils are industrial products including fuels, but not food or feed, made from renewable agricultural or forestry resources. Seed oils are currently one of the most common sources

of biobased oils and among the various seeds from which seed oils are derived, soybeans are clearly in greatest production worldwide and the United States has the highest soybean production rate, followed by Brazil [5].

Tagaya and Tamura compared the quench severity of different vegetable oils including soybean, rapeseed and castor oils with mineral oils and fish/animal oils with respect to fluid source and viscosity and oxidative stability for various naturally derived fluids [6]. Fujimura and Sato followed this work in 1963 and concluded that the performance of soybean and rapeseed oil were essentially equivalent [7].

Oxidative stability performance improvements of vegetable oils can be achieved by chemical [8] or genetic modifications [9] or by process improvements such as winterization and partial hydrogenation [10]. Winterization (fractionation) is performed to remove crystallized fats and improve the pour point of the base oil. The performance objective is to reduce the linolenic and linoleic ester content of the vegetable oil to increase the oxidative stability making the resulting vegetable oil more suitable for use in industrial applications [11]. Genetic engineering has produced soybean oil with > 85% oleic acid ester contents [8]. There are, however, a number of substantial problems with genetic engineering to reduce polyunsaturation including costs associated with regulatory approval.

Totten et. al. reported the results of cooling curve, hardenability, heat transfer, and wettability characterization studies conducted with crude and partially hydrogenated and winterized soybean oils [10]. Although there are various references to the quenching performance of soybean oil, and other vegetable oils such as the work reported by Prabhu [12,13], with the exception of Tagaya and Tamura [13] and Canale et.al. [14], and Souza et.al. [15] there have been relative few reports on the effect of the oxidative degradation and stabilization by antioxidant addition on quenching performance.

The objective of this work was to systematically examine the degradation of quenching performance of soybean oil with and without the addition of antioxidants. This discussion will include an overview of soybean oil structure, degradation and stabilization.

EXPERIMENTAL

The soybean oil used for this work was purchased at the local market in Sao Carlos, Brazil and was used in the as-purchased condition. Palm oil was obtained from Campestre Indústria e Comércio de Óleos Vegetais Ltda. The quenching performance of these oils was compared to commercial petroleum quenching oils designated as Houghto-Quench G (HG) and Houghto-Quench KM (HKM) by Houghton Internacional.

Two antioxidants were used for this work are Irganox® L109 obtained from BASF International and Propyl Gallate obtained from Sigma-Aldrich. Propyl gallate and Irganox® L109 were added at concentrations of 1% and 0.5 wt% to soybean and palm oils and designated as shown in **Table 1**. The homogenization of the antioxidant in oils was achieved by stirring (and heating, if necessary) at room temperature (~20°C) for 10 minutes.

Table 1 – Nomenclature for the fluids.

Fluids Evaluated	Name Used
Soybean oil pure	SO
Soybean Oil + Antioxidants	SO _{AX}
Soybean Oil + Aging	SO _{ANG}
Soybean Oil + Antioxidants + Aging	SOA _{ANG}
Palm Oil pure	PO
Palm Oil + Antioxidants	PO _{AX}
Palm Oil + Aging	PO _{ANG}
Palm Oil + Antioxidants+ Aging	POA _{ANG}

Kinematic viscosities of the samples were determined using an automatic viscometer manufactured by Herzog HYU 481 model with calibrated capillary tube of the Ubbelohde type according to ASTM D445-12. The samples in new and aged conditions were injected into the capillary tubes in a thermostated bath for 15 minutes at pre-set temperatures of 40 and 100 °C. The kinematic viscosity provided by the equipment is calculated using the ASTM D2270-10e1.

Thermo-oxidative stability was determined based on the standards ASTM D6186-08 and ASTM E2009-08 using an exploratory differential calorimeter DSC Q2000 coupled to a Q20P pressure cell, both manufactured by TA-Instruments. The oxidative onset temperatures (OOT) were obtained with about 3 mg of sample under an atmosphere of oxygen and pressure 300 psi at a heating rate of 10 °C.min⁻¹, and in the temperature range 40-300 °C.

The iodine value is an important measure which indicates the degree of unsaturation present in the chemical structure of the oils. In the classical (Wijs) method, the iodine value is expressed as the amount of iodine absorbed per 100 g of oil [15]. However, in this work the iodine value was calculated from ¹H NMR spectra [16].

The vegetable oils spectra of nuclear magnetic resonance (¹H NMR) spectra of the vegetable oils was obtained using an Agilent Premium Shielded 400/54 spectrometer operating at 500 MHz and a temperature of 26 °C. The tetramethylsilane (TMS) was used as internal reference. Samples were prepared by dissolving 10 mg of the oil in 600 uL of deuteriochloroform (CDCl₃). The spectral acquisition parameters were: 15 second relaxation time, 90° pulse (11.7 sec), 5.112 second acquisition time, spectral width of 6410 Hz and 32 transients for each free induced decay.

Cooling curves were obtained in triplicate under unagitated conditions according ASTM D6200 at bath temperatures of 60 and 100 °C. The cooling curves used for this work were obtained by averaging the experimental curves. This test method is based on the 12.5 mm dia. X 60 mm cylindrical INCONEL 600. After heating the probe in a furnace to 850 °C (1562 °F), it was then manually and rapidly immersed into 2000 mL of the oil to be tested which was contained in a tall-form stainless steel beaker. The probe temperature and cooling times are recorded at selected time intervals to establish a cooling temperature versus time curve.

RESULTS AND DISCUSSION

Soybean and Palm Oil Structure and Stability

Thermo-oxidative stability of a vegetable oil is dependent on the fatty ester composition of the triglyceride structure. Increasing amounts of unsaturation in the fatty ester structure leads to increased oxidative instability. Kodali [17] reported that the relative rate of oxidation increases as the number of double bonds in conjugation with each other increases in the following relative order: stearic (1) < oleic (10) < linoleic (100) < linolenic (200) shown in **Fig 1**.

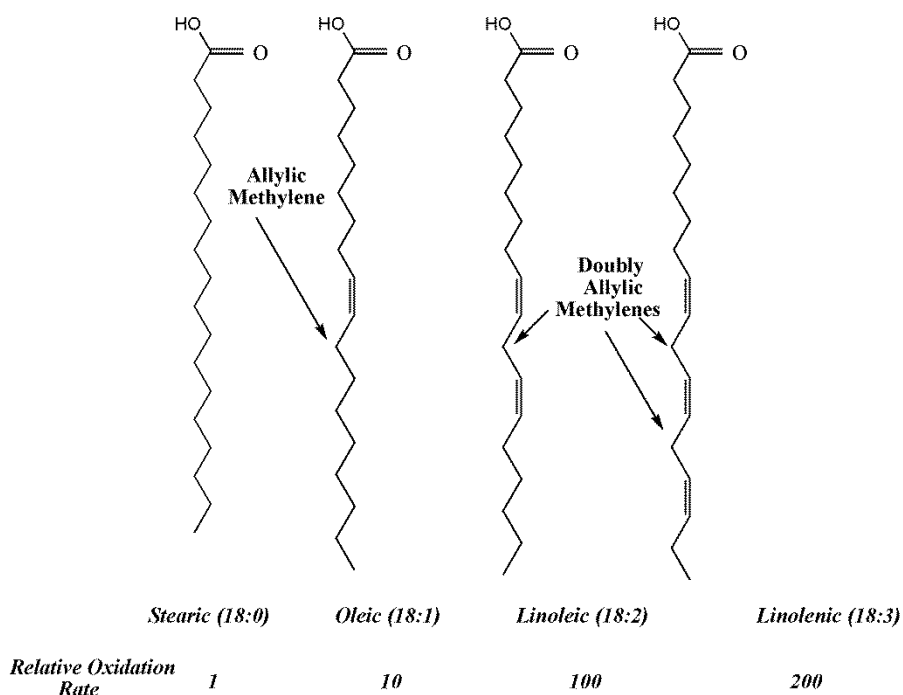


Figure 1 – Comparison of the relative oxidation rates of the most common fatty acid components of various seed oils.

The composition of the soybean and palm oil used for this work was determined by ^1H NMR using the method reported earlier by Miyake, et.al. [18]. The results of this analysis are shown in **Table 2** and are consistent with a published composition. The iodine number and molecular weight was also determined by ^1H NMR [16]. These data show that soybean oil exhibits substantially higher concentrations of conjugated unsaturated fatty acids linoleic acid and linolenic acid as well as total unsaturation relative to palm oil. Based on the relative reactivities shown in Fig. 1, it is expected that without the use of antioxidants, soybean oil would be much less oxidatively stable than palm oil.

Table 2 – Unsaturation of soybean and palm oil determined from ^1H NMR spectra of vegetable oils.

Fatty acid component	Fatty acid (%)	
	Soybean	Palm
Linolenic acid	5.12	1.80
Linoleic Acid	52.18	3.82
Oleic Acid	24.05	49.26
Saturated acids	15.90	45.18
Iodine value (cg l/g)	124.74	57.36
Average molar mass (g/mol)	898.38	861.18

PDSC (Pressurized Differential Scanning Calorimetry) is one of the main techniques used for determining the oxidative state of the fatty acids. Compared to traditional analytical methods, PDSC exhibits greater precision and sensitivity and smaller sample quantities with substantially faster analysis speeds [19,20].

Table 3 shows the PDSC results for soybean and palm oil with the addition of antioxidants and different concentrations. The OOT (oxidation onset temperature) of the vegetable oils without antioxidants showed significant improvements with the addition of different antioxidants. As expected, palm oil, with and without antioxidants, exhibits better thermal oxidative stability than soybean oil. In addition to improved oxidative stability, the data suggests that there is synergy between the some combinations.

Table 3 – Oxidation Onset Temperature (OOT) by PDSC.

<i>Antioxidants concentration</i>	<i>OOT (°C)</i>	
	<i>Palm</i>	<i>Soybean</i>
Pure	182.91	165.85
1% Irganox® L109	198.85	176.67
1% Irganox® L109 + 0.5% BHA	207.43	190.24
1% Irganox® L109 + 0.5% TBHQ	214.57	186.34
1% Irganox® L109 + 0.5% GP	217.66	195.77
0.5% Propyl Galate	208.91	175.29

Kinematic Viscosity Results Before Aging

Fluid viscosities typically decrease with increasing temperature. The commercial petroleum quenching oils HG and HKM exhibit generally lower viscosities than soybean oil or palm oil at all temperatures evaluated. The SO and SO_{AX} fluids (see **Table 4**) exhibited the lowest viscosity at 40 °C relative to PO and PO_{AX}. This behavior is explained by the concentration of saturated and monounsaturated fatty acids, the lower the concentration of these acids, the lower the oil viscosity [21]. The SO_{AX} and PO_{AX} formulations exhibited viscosities similar to the uninhibited vegetable oils from which they were formulated. The addition of Irganox® L109 and propyl gallate antioxidants did not affect the viscosity. The **Table 4** shows the variation of viscosity with the temperature and the viscosity index.

Table 4 – Viscosity-temperature properties comparison of palm and soybean fluids and petroleum-based quenchants and viscosity index (VI).

<i>Temperature (°C)</i>	<i>Fluids</i>				<i>Mineral fluids</i>	
	<i>SO</i>	<i>SO_{AX}</i>	<i>PO</i>	<i>PO_{AX}</i>	<i>HG</i>	<i>HKM</i>
40	31.51	31.58	40.82	40.83	25.29	13.67
60	17.84	17.78	17.15	17.12	13.11	7.83
100	7.82	7.89	8.21	8.29	4.82	3.22
<i>Viscosity index (VI)</i>	235	238	182	185	112	100

Viscosity index (VI) expresses the viscosity change with respect to temperature. The higher the VI, the less viscosity changes with temperature. A comparison of the viscosity index of the fluids studied is shown in **Table 4**. The SO, SO_{AX} and palm oil exhibited the highest VI values, indicating the least

viscosity variations with temperature. Petroleum oils are well known to exhibit comparatively poorer VI values.

Cooling curves quantification and Results

The cooling time-temperature curves for the various vegetable oil compositions and commercial petroleum oil derived quenchants were obtained at 60 °C and 100 °C and the quantitative cooling curve parameters discussed in ASTM D6200 were calculated from the time-temperature data files. A summary of these parameters and the values obtained is provided in **Table 5**.

Table 5 - Cooling parameters obtained by ASTM D6200 at 60 °C, no agitation

<i>Cooling Curves Parameters 60 °C</i>	<i>Fluids</i>				<i>Mineral fluids</i>	
	<i>SO</i>	<i>SO_{AX}</i>	<i>PO</i>	<i>PO_{AX}</i>	<i>HG</i>	<i>HKM</i>
<i>T_{A-B} (°C)</i>	790	786	683	704	715	770
<i>t_{A-B} (s)</i>	5.0	6.6	16.6	14.5	14.4	8.8
<i>CR_{A-B} (°C/s)</i>	57	44	26	28	20	35
<i>T_{max} (°C)</i>	699	688	591	593	625	582
<i>t_{max} (s)</i>	7.6	9.7	19.6	18.3	17.6	14.0
<i>CR_{max} (°C/s)</i>	92	93	88	92	102	115
<i>CR_{700°C} (°C/s)</i>	92	92	26	28	38	68
<i>CR_{300°C} (°C/s)</i>	6.6	6.6	28	27	6	34
<i>CR_{200°C} (°C/s)</i>	2.6	2.6	9.3	6.0	2.6	10

For the two petroleum oil quenchants evaluated, the Leidenfrost temperatures were 715 °C and 770 °C for HG and HKM respectively. Lower Leidenfrost temperatures mean that the probe had to cool longer before the vapor could rupture, thus petroleum oils exhibited substantially longer vapor blanket cooling behavior. As expected, the “super-accelerated” petroleum oil quenchant (HKM) exhibited much shorter vapor blanket rupture times than the more “conventional” petroleum oil quenchant, HG. The HKM fluid also exhibited a comparatively higher maximum cooling rate (CR_{max}) which is in agreement with the data provided from the manufacturer.

The SO and SO_{AX} fluids exhibited the shortest vapor blanket behavior as evidenced by higher T_{A-B} (Leidenfrost temperature) temperatures. The vapor blanket of for SO ruptured at 790 °C and after 5.0 seconds and for the SO_{AX} fluid, at 786 °C, at 6.6 seconds. The data suggests that the presence of an antioxidant delays vapor blanket rupture by approximately 2 seconds under these particular cooling conditions. The vapor blanket rupture times for SO and SO_{AX} is almost half of the time observed for the petroleum oil quenchant HG.

The PO and PO_{AX} palm oil-based fluids exhibited comparatively longer vapor blanket behavior based on their Leidenfrost temperatures, 683 °C and 704 °C, respectively than did the soybean oil derived fluids SO and SO_{AX} vapor blanket and occur. Analyses of the cooling rate data illustrate that higher fluid viscosities exhibit better wettability and consequently times longer vapor blanket cooling behavior [12].

The cooling rate at 700 °C is an important cooling parameter. It is desirable to maximize the cooling rate at this temperature to minimize pearlite formation. The SO and SO_{AX} fluids exhibited considerably greater CR_{700°C} values of the fluids evaluated. This behavior indicates that the cooling mechanism is primarily by convection. Vegetable oils have the lowest CR_{max} values. The results show that vegetable oils exhibit substantially different physico-chemical characteristics than petroleum oils which results in very different cooling performance.

Typically, it is desirable to minimize the CR_{300°C} and CR_{200°C} values since minimization of these values also minimize potential for steel cracking and distortion. In this study, the highest CR_{300°C} and CR_{200°C} values were obtained with the PO, PO_{AX} and HKM fluids. The SO exhibited a relatively low cooling rate in CR_{300°C} and CR_{200°C} which was equivalent to the HG petroleum oil.

CONCLUSIONS

The results of the work performed in this study have shown that based on PDSC measurements palm oil exhibits significantly greater thermal-oxidative stability than soybean oil which is attributable to the amount and type of unsaturation in the two oils. Palm oil not only has less total unsaturation but also relative little polyunsaturation as is present in soybean oil. In addition, not only do antioxidants, namely: propyl gallate and Irganox® L109 provide substantial stabilization of the uninhibited oils but also when used together, there appears to be a significant synergistic effect.

Fluid viscosity studies show that the presence of antioxidants exhibit little, if any, significant effect on kinematic viscosity. The viscosities of the vegetable oil-based fluids is greater than that exhibited by the commercial quench oils evaluated; HG and HKM. However, all of the vegetable oil-based fluids exhibited the highest viscosity indices which indicate that the fluid viscosities of the petroleum oil-based fluids are much more sensitive to variations in temperature.

Cooling curve analyses show that, as expected, the “super-accelerated” petroleum oil quenchant, HKM, exhibited shorter vapor blanket cooling properties than the conventional petroleum oil quenchant, HG. Furthermore, soybean oil-based fluids, in particular exhibited very comparatively shorter vapor blanket cooling than either palm oil-based fluids or the petroleum oils. This indicates that the cooling mechanism for the vegetable oil-based fluids is predominantly convection. However, overall cooling rates and times are faster with the vegetable oil-based fluids.

Further work is being completed which will confirm the effect of vegetable oil – antioxidant formulations on fluid aging and viscosity change and its impact on quenchant performance.

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